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Co-Occurrence Patterns of Gaseous Air Pollutant Pairs at Different Minimum Concentrations in the United States (Journal Version)

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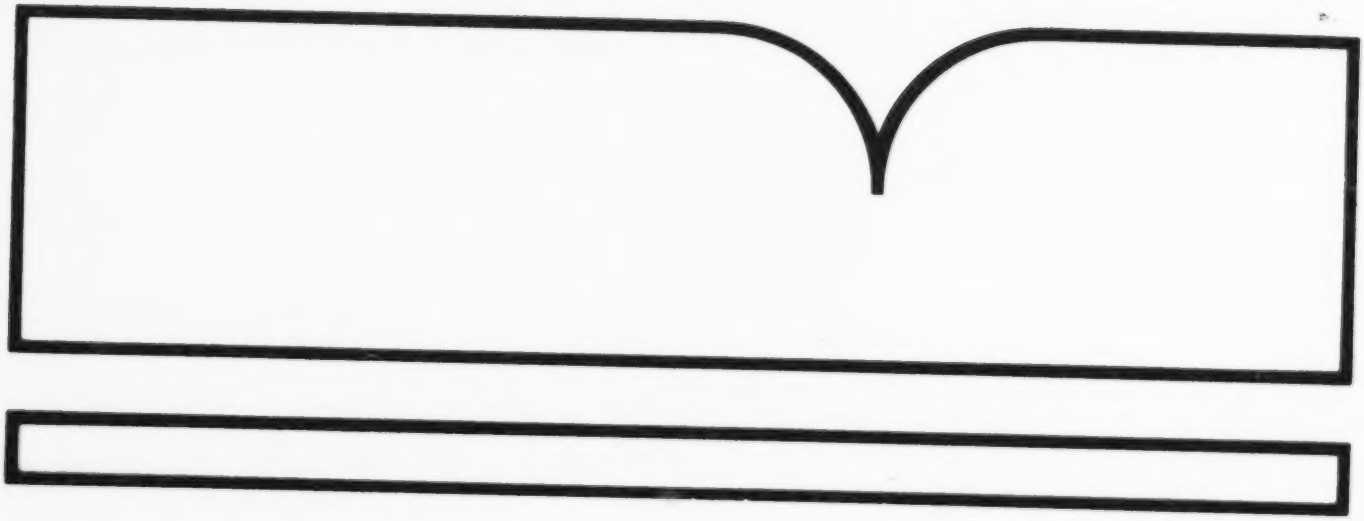

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16. ABSTRACT

The frequency of co-occurrences for SO_2/NO_2, SO_2/O_3 and O_3/NO_2 at rural and remote monitoring sites in the United States was characterized for the months of May-September for the years 1978-1982. Minimum hourly concentrations of 0.03 and 0.05 ppm of each gas were used as the criteria for defining a 'co-occurrence'. The objectives of this study were to: (1) identify the types of co-occurrence patterns and their frequency; (2) identify whether the frequency of hourly simultaneous co-occurrences increased substantially when the minimum concentration was lowered (e.g. from 0.05 to 0.03 ppm) for each pollutant; and (3) determine whether the frequency of co-occurrences showed large year-to-year variation. For all pollutant pairs and co-occurrence thresholds (i.e. 0.03 and 0.05 ppm), the frequency of daily and hourly co-occurrences was low for most sites. Year-to-year variability was found to be insignificant; most of the monitoring sites experienced co-occurrences of any type less than 12% of the 153 days. Based on our observations, researchers attempting to assess the potential effects of SO_2/NO_2, SO_2/O_3 and O_3/NO_2 in the United States should construct simulated exposure regimes so that (1) hourly simultaneous and daily simultaneous-only co-occurrences are fairly rare and (2) when co-occurrences are present, complex-sequential and sequential-only co-occurrence patterns predominate.

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CO-OCCURRENCE PATTERNS OF GASEOUS AIR POLLUTANT PAIRS AT DIFFERENT MINIMUM CONCENTRATIONS IN THE UNITED STATES

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Abstract—The frequency of co-occurrences for SO_2/NO_2, SO_2/O_3 and O_3/NO_2 at rural and remote monitoring sites in the United States was characterized for the months of May–September for the years 1978–1982. Minimum hourly concentrations of 0.03 and 0.05 ppm of each gas were used as the criteria for defining a 'co-occurrence'. The objectives of this study were to: (1) identify the types of co-occurrence patterns and their frequency; (2) identify whether the frequency of hourly simultaneous co-occurrences increased substantially when the minimum concentration was lowered (e.g. from 0.05 to 0.03 ppm) for each pollutant; and (3) determine whether the frequency of co-occurrences showed large year-to-year variation. For all pollutant pairs and co-occurrence thresholds (i.e. 0.03 and 0.05 ppm), the frequency of daily and hourly co-occurrences was low for most sites. Year-to-year variability was found to be insignificant; most of the monitoring sites experienced co-occurrences of any type less than 12% of the 153 days. Based on our observations, researchers attempting to assess the potential effects of SO_2/NO_2, SO_2/O_3 and O_3/NO_2 in the United States should construct simulated exposure regimes so that (1) hourly simultaneous and daily simultaneous-only co-occurrences are fairly rare and (2) when co-occurrences are present, complex-sequential and sequential-only co-occurrence patterns predominate.

Key word index: Ambient exposure regimes, complex-sequential co-occurrence, co-occurrence, hourly occurrences, minimum concentrations, ozone, nitrogen dioxide, sequential-only co-occurrence, simultaneous co-occurrence, simultaneous-only co-occurrence, sulfur dioxide, vegetation effects.

1. INTRODUCTION

While most studies assessing the effects of gaseous air pollutants on vegetation have applied O_3, SO_2 or NO_2 individually, there have been increasing efforts to measure the effects of pollutant mixtures on vegetation. In these investigations, pollutant combinations co-occurred for several hours a day over an extended period (e.g. Tingey *et al.*, 1971; Oshima, 1978; Ashenden, 1979; Ashenden and Williams, 1980; Heggestad and Bennett, 1981; Foster *et al.*, 1983; Heagle *et al.*, 1983; Thompson *et al.*, 1984).

While the pollutant exposure regimes used in the cited studies provide insight into physiological processes and the nature of plant responses, they are not typical of ambient air quality in many agriculturally-related areas in the United States. Lefohn and Tingey (1984) examined several air quality data bases for the United States and showed that (1) the occurrence of pollutant pairs together (SO_2/NO_2, SO_2/O_3 or O_3/NO_2), at hourly mean concentrations equal to or greater than 0.05 ppm, lasted only a few hours per episode and (2) the time interval between episodes was generally great (weeks, sometimes months). The investigators used hourly mean data from the (1) 1981 Environmental Protection Agency's Storage and Retrieval of Aerometric Data (SAROAD) data base, (2) 1978 and 1979 Electric Power Research Institute's (EPRI) Sulfate Regional Experiment (SURE) and Eastern Regional Air Quality Study (ERAQS) data base, and (3) 1978–1982 Tennessee Valley Authority's (TVA) data base.

The Lefohn and Tingey (1984) analysis included a large number of SAROAD urban monitoring sites along with rural sites and used a 0.05 ppm threshold to identify the number of hourly simultaneous co-occurrences. Including urban monitoring sites in the analyses may not have adequately characterized the co-occurrence patterns associated with pollutant mixtures in agricultural areas. The 0.05 ppm threshold originally used may have been at such a level that large numbers of simultaneous co-occurrences between 0.03 ppm and 0.05 ppm would not have been identified. Although Lefohn and Tingey (1984) explored the hourly simultaneous co-occurrences of pollutant pairs, episodes can occur independently on a given day

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without appearing simultaneously. If such non-simultaneous occurrences of pollutant pairs are frequent, then pollutants exhibiting such patterns may affect vegetation at a lower concentration than they would if the pollutants appeared by themselves.

This paper extends the original analysis of Lefohn and Tingey (1984) by (1) using only co-monitored sites designated as rural and remote; (2) identifying the different types of pollutant pair co-occurrence patterns and their frequency; (3) identifying whether the frequency of hourly simultaneous co-occurrences increased substantially when the minimum concentration was lowered (e.g. from 0.05 to 0.03 ppm) for each pollutant; and (4) determining whether the frequency of co-occurrences showed large year-to-year variation.

2. METHODS

The primary purpose of this paper was to characterize air pollutant mixture regimes that might impact agricultural crops. The analysis of air quality data was, therefore, restricted to the 5-month growing season of May–September. The only ambient air quality sites included in the analyses were those that (1) were designated as rural or remote by the site operators; (2) had hourly mean data reported for at least two pollutants; (3) had at least 3 months of data concurrently collected for each pollutant for the 5-month period; and (4) had at least 3 months of data collected for each pollutant where greater than 50% of the hours per month were reported.

Data used in the investigation included hourly averaged (1) EPA SAROAD data from 1978 to 1982, (2) EPRI-SURE and -ERAQS data for 1978 and 1979, and (3) TVA data from 1978 to 1982. The SAROAD data base was established to collect and disseminate air monitoring data obtained by local, state and Federal monitoring networks. The monitoring stations in the EPRI-SURE and -ERAQS programs were located primarily in the northeastern United States to determine the relationship between emissions of SO_2 and the distribution and concentration of its reaction products. The TVA monitoring sites were associated with source and trend characterization locations. The nine EPRI and five TVA monitoring sites used in the analysis are listed (Table 1).

Many of the rural and remote monitoring sites used in the study recorded data over a multiple year period. In this analysis, multiple years of data at a site are treated independently. Thus, if the same monitoring site had 5 years of data reported, there were five sets of data used. The number of sites used from each data base (by year) is shown by pollutant pair (Table 2).

Pollutant pairs can occur at or above a threshold concentration either together or separated from one another. To characterize the different types of co-occurrence patterns, we have grouped the air quality data within a 24-h period starting at 0000 h and ending at 2359 h. Patterns that showed air pollutant pairs appearing at the same hour of the day at concentrations equal to or greater than a minimum hourly

Table 1. EPRI and TVA air quality monitoring sites used in the analysis

Site	Years
EPRI-SURE/-ERAQS*	
Montague, Massachusetts	1978–1979
Scranton, Pennsylvania	1978–1979
Indian River, Delaware	1978–1979
Duncan Falls, Ohio	1978–1979
Rockport, Indiana	1978–1979
Giles County, Tennessee	1978–1979
Wayne, Indiana	1978–1979
Research Triangle Park, North Carolina	1978–1979
Lewisburg, West Virginia	1978–1979
TVA	
Giles County, Tennessee	1980–1982
Land Between the Lakes, Tennessee	1982
Murphy Hill, Alabama	1980
Paradise 21, Kentucky	1979–1982
Saltillo, Tennessee	1979–1980.

* The EPRI-SURE and -ERAQS data provided hourly NO and NO_x concentrations. In our analysis, it was assumed that NO_x could be substituted for NO_2 concentrations; using NO_x as a surrogate for NO_2 overestimates the NO_2 concentration.

Table 2. Summary by year of the number of sites from each data base included in the analysis

	1978	1979	1980	1981	1982	Total
SO_2/NO_2						
SAROAD	9	26	8	19	21	
EPRI	9	9	—	—	—	
TVA	0	1	4	1	3	
Total	18	36	12	20	24	110
SO_2/O_3						
SAROAD	10	21	9	15	13	
EPRI	9	9	—	—	—	
TVA	0	1	3	1	3	
Total	19	31	12	16	16	94
O_3/NO_2						
SAROAD	6	12	7	12	10	
EPRI	9	9	—	—	—	
TVA	0	0	3	0	3	
Total	15	21	10	12	13	71

The (—) notation designates that EPRI monitoring data were not collected during the specified year.

mean value were defined as a 'simultaneous-only' daily co-occurrence. Figure 1a shows an example of a simultaneous-only co-occurrence during which the hourly concentrations of both pollutants were at or above a minimum concentration of 0.05 ppm between 1000 and 1300 h. The hourly concentrations did not occur together at or above 0.05 ppm during any other time over the 24-h period.

When pollutant pairs occurred at or above a minimum concentration during the 24-h period without occurring at the same hour, 'sequential-only' co-occurrence was defined (Fig. 1b). NO_2 levels were above the minimum concentration (0.05 ppm) for several hours during the early morning. At no time during this period were the SO_2 concentrations above the threshold level. During the period when NO_2 hourly concentrations were below 0.05 ppm, there were several hours when SO_2 hourly concentrations exceeded the 0.05 ppm minimum concentration. In the late afternoon and evening, NO_2 hourly concentrations were > 0.05 ppm, but the SO_2 hourly concentrations were < 0.05 ppm.

During a 24-h period, if the pollutant pair occurred at or above the minimum level at the same hour of the day and at different hours during the period, the co-occurrence pattern was defined as 'complex-sequential' (Fig. 1c). The NO_2 hourly concentration equalled or exceeded the minimum concentration (0.05 ppm) during the early morning before decreasing during mid-day to concentrations below the minimum con-

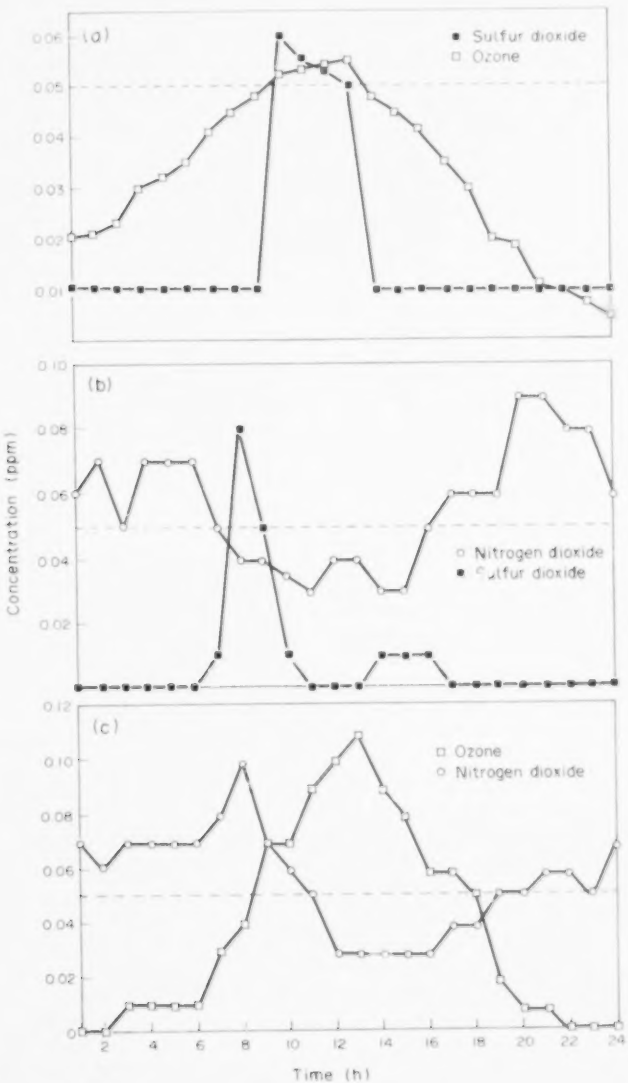

Fig. 1. Examples of different forms of co-occurrences: (a) simultaneous-only co-occurrence of SO_2/O_3 at concentrations $\geq$ 0.05 for a set of hourly data; (b) sequential-only co-occurrence of SO_2/NO_2 at concentrations $\geq$ 0.05 ppm; (c) complex-sequential co-occurrence of O_3/NO_2 at concentrations $\geq$ 0.05 ppm. The horizontal dash line designates the minimum concentration (0.05 ppm).

centrations and then subsequently increasing above the level during the evening. As the NO_2 concentration decreased, the O_3 concentration increased, reaching a maximum at 1300 h. Both pollutants equalled or exceeded the minimum concentration between 0900 h and 1100 h. As the O_3 concentration continued to increase, the NO_2 level dropped below the minimum level.

The daily co-occurrence patterns were examined at two different minimum concentrations (i.e. 0.03 and 0.05 ppm) for the 24-h period. A co-occurrence was not indicated if one pollutant exceeded the minimum concentration just before midnight and the other pollutant exceeded the minimum concentration just after midnight. We believe this omission to be minor because pollutant mixtures involving O_3 (i.e. SO_2/O_3 and O_3/NO_2) would not normally experience co-occurrences in the late evening or early morning at agriculturally-related sites due to the photochemistry involved in O_3 production. In addition, if the hourly occurrences of either SO_2 or NO_2 at or above the minimum concentration were infrequent over the 5-month period, the number of days with SO_2/NO_2 co-occurrences occurring in the late evening or early morning would be small.

Daily co-occurrence patterns were characterized by tabulating the number of days of total co-occurrences. The total number of co-occurrences was segregated into the individual subcomponents (i.e. simultaneous-only, sequential and complex-sequential co-occurrences). The percentage of sites experiencing more than 19 days of co-occurrences was determined over the 5-month period for any given year. The results were tabulated by year and summarized in this paper as a range of percentage values experienced over the 5-year period. Significant year-to-year variation was investigated by performing an analysis of variance on the proportions of the ratios of daily co-occurrences to the number of monitoring days over the 153-day period. An arc sine transformation was used to transform the binomial proportions prior to the analysis of variance. In the transformed scale, the variances are proportional to the number of available days, which varied from 62 to 153.

Besides characterizing the types of co-occurrences within a 24-h period, hourly simultaneous co-occurrence patterns were summarized to (1) identify whether the application of different minimum concentration levels modified the conclusions reached by Lefohn and Tingey (1984) and (2) quantify the year-to-year variability. These hourly simultaneous co-occurrence results were tabulated by year for the 5-month period and reported as a range of percentage values experienced over the 5-year period.

3. RESULTS

3.1. *Daily occurrences of individual pollutants*

The frequency of occurrence of each pollutant (i.e. O_3, SO_2 or NO_2) limits the number of possible co-occurrences each can experience with the other two pollutants. For example, if the number of days with SO_2 hourly concentrations $\geq$ a minimum concentration (e.g. 0.03 ppm) was small, the number of days with co-occurrences of SO_2 with O_3 or NO_2 would also be small. To put into perspective the potential number of co-occurrences, we characterized the number of days with hourly occurrences equal to or greater than 0.03 ppm and 0.05 ppm for each of the three pollutants.

Daily occurrences of O_3 with hourly concentrations $\geq$ 0.03 ppm were frequent (Fig. 2a). Out of a maximum number of 153 days (5 months), 95% of all the sites for all years experienced 80 or more days (52% of the total) when O_3 was $\geq$ 0.03 ppm. On the other hand, at any specific site, the number of days with SO_2 and NO_2 hourly concentrations $\geq$ 0.03 ppm was small (Figs 2b and 2c). Including data for all years, only 3% of the sites had 80 or more days when the SO_2 hourly concentrations were at or above the 0.03 ppm level (56% of the sites had fewer than 20 days). Seventeen percent of the sites had 80 or more days when the NO_2 hourly concentrations were $\geq$ 0.03 ppm (51% of the sites experienced fewer than 20 days). When the minimum concentration was raised to 0.05 ppm, as anticipated, fewer days with O_3, SO_2 and NO_2 occurrences were experienced.

3.2. *Daily co-occurrences of pollutant pairs*

SO_2/NO_2. Only a few days with any type of SO_2/NO_2 co-occurrence (i.e. simultaneous-only, sequential-only and complex-sequential) were observed (Fig. 3). Using a minimum concentration of 0.03 ppm, a review of the data for any May–September period indicated that only 5–33% of the sites in any given year experienced more than 19 days (13% of the total number of days over a 5-month period) with any type of co-occurrences. During the 5-year period, few sites experienced simultaneous-only co-occurrences. Of the sites reporting days with simultaneous-only co-occurrences, one experienced 14 days; the remainder experienced fewer than 5. While the percentage of monitoring sites with any type of SO_2/NO_2 co-occurrence was low, the percentage experiencing more than 19 days of complex-sequential co-occurrences was higher than for the sequential-only co-occurrences (Table 3).

Raising the minimum concentration to 0.05 ppm further reduced the small number of days with any type of co-occurrence (Table 3). Using a minimum concentration of either 0.03 or 0.05 ppm, no significant year-to-year variation was found at the 0.05 level (Table 4). Only a few sites experienced days with simultaneous-only co-occurrences. The small number of sites that did experience days with simultaneous-only co-occurrence reported < 5. None of the monitoring sites experienced more than 19 days of sequential-only co-occurrences. The percentage of sites that experienced more than 19 days of complex-sequential co-occurrences in any given year ranged from 0 to 10% (Table 3).

SO_2/O_3. For the SO_2/O_3 combination, when the data were analyzed using a minimum concentration of 0.03 ppm, 24–43% of the sites experienced in any given year more than 19 days with any type of co-occurrence (Fig. 4a). Most experienced no days with simultaneous-only co-occurrences. Of the few that did, only 1 day was recorded. Most sites experienced either days with sequential-only or complex-sequential co-occurrences (Table 3). The complex-sequential co-occurrences were most frequent with 15–37% of the monitoring sites experiencing more than 19 days of complex-sequential co-occurrences and 0–5% more

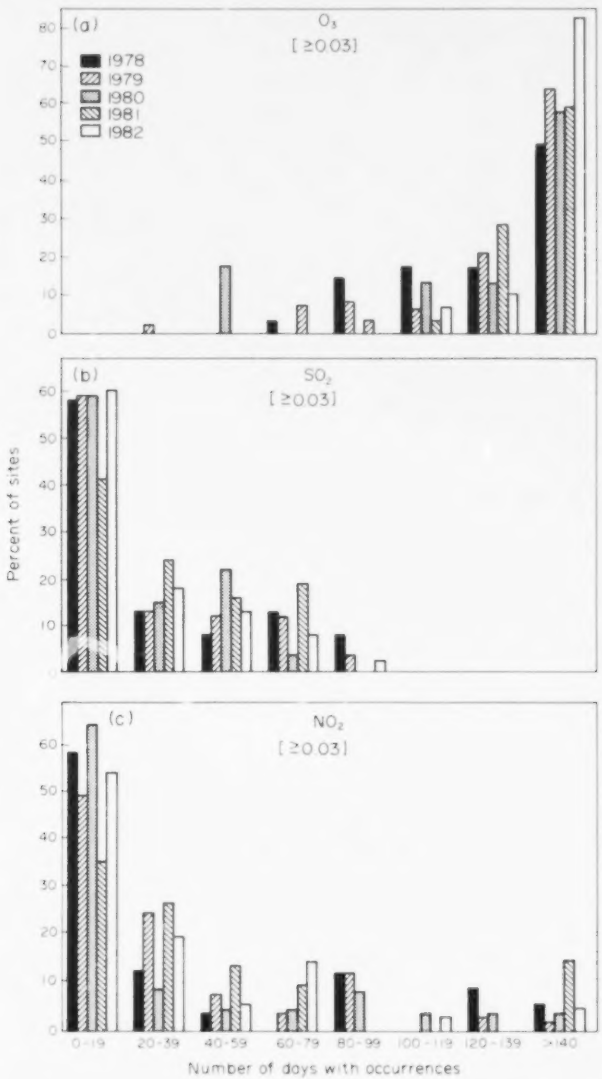

Fig. 2. Number of days with occurrences at a concentration ≥ 0.03 ppm for May–September for: (a) O_3; (b) SO_2; (c) NO_2.

than 19 days with sequential-only co-occurrences (Table 3).

When the minimum concentration was raised to 0.05 ppm, 6–22 % of the sites experienced in any given year more than 19 days with any type of co-occurrence (Fig. 4b). As found for the SO_2/NO_2 co-occurrences, using a minimum concentration of either 0.03 or 0.05 ppm resulted in no significant year-to-year variation at the 0.05 level (Table 4). Except for one site, all other stations experienced no simultaneous-only co-occurrences. The one station reported 1 day with a simultaneous co-occurrence. The percentage of monitoring sites experiencing more than 19 days with sequential-only co-occurrences at the 0.05 ppm level was similar to that experienced using the 0.03 ppm level (Table 3); the percentage range of monitoring sites experiencing more than 19 days with complex-sequential co-occurrences was reduced (Table 3).

O_3/NO_2. Using a minimum concentration of 0.03 ppm for the O_3/NO_2 combination, 37–61 % of the sites experienced in any given year more than 19 days with any type of co-occurrence (Fig. 5a). During the May–September period for any year, there were never more than 3 days at any site with simultaneous-only co-occurrences. Sequential-only co-occurrences predominated over the complex-sequential co-occurrences (Table 3).

When the minimum concentration was raised to

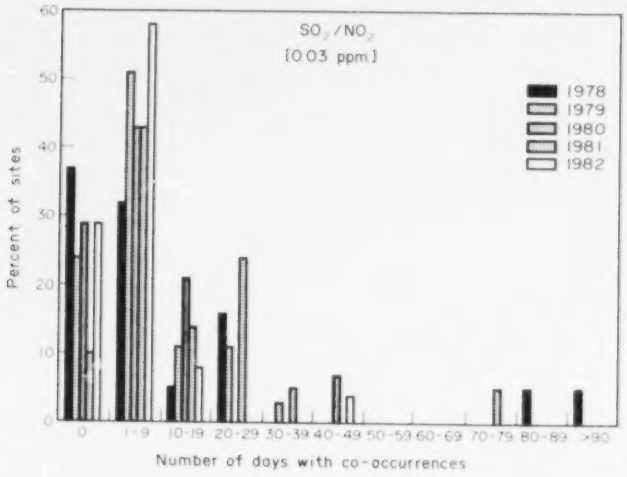

Fig. 3. Daily co-occurrence patterns of SO_2/NO_2 for May–September at a concentration ≥ 0.03 ppm.

Table 3. Mean of percent of monitoring sites experiencing >19 days of co-occurrences at minimum concentrations ≥ 0.03 ppm and ≥ 0.05 ppm for May–September 1978–1982.

Pollutant	Minimum concentration 0.03 ppm			Minimum concentration 0.05 ppm		
	Simultaneous-only	Sequential-only	Complex-sequential	Simultaneous-only	Sequential-only	Complex-sequential
SO_2/NO_2	0 (0)	2 (0–5)	9 (4–14)	0 (0)	0 (0)	3 (0–10)
SO_2/O_3	0 (0)	1 (0–5)	25 (15–37)	0 (0)	2 (0–5)	4 (0–9)
O_3/NO_2	0 (0)	36 (31–45)	25 (19–31)	0 (0)	19 (14–23)	9 (0–23)

The percent of sites that met the above criteria during the 5-month period for each year is calculated and the mean over the period 1978–1982 was determined. The range of percentages experienced is designated in ( ).

Table 4. Results of weighted ANOVA performed on arc sines of proportions testing for yearly differences

Pollutant pair	Minimum conc.	*P*-value	MSE	1978	1979	1980	1981	1982	Overall
O_3/NO_2	0.03	0.943	26.1	0.263	0.298	0.388	0.375	0.298	0.316
O_3/NO_2	0.05	0.700	15.9	0.094	0.083	0.098	0.166	0.046	0.091
SO_2/O_3	0.03	0.862	7.9	0.141	0.092	0.112	0.121	0.098	0.109
SO_2/O_3	0.05	0.794	3.8	0.056	0.033	0.032	0.036	0.028	0.036
SO_2/NO_2	0.03	0.106	4.7	0.077	0.038	0.041	0.094	0.028	0.049
SO_2/NO_2	0.05	0.120	1.4	0.022	0.009	0.007	0.016	0.004	0.010

* MSE, Mean standard error.

0.05 ppm, 15–23% of the sites in any given year had more than 19 days of any type of co-occurrence (Fig. 5b). Using an analysis of variance, no significant year-to-year variation was found at the 0.05 level when a minimum concentration of either 0.03 or 0.05 ppm was used (Table 4). Only one site experienced a simultaneous-only co-occurrence, and that happened only once. Sequential-only co-occurrences continued to predominate over the percentage of complex-sequential co-occurrences (Table 3). However, at the 0.05 ppm level, both types of co-occurrences were infrequent (Table 3).

In contrast to our SO_2/NO_2 and SO_2/O_3 co-occurrence results, several sites, using a minimum concentration of 0.05 ppm, experienced more than 90 days with O_3/NO_2 co-occurrences over the 5-month period (Fig. 5b). The sequential-only and complex-sequential co-occurrences for O_3/NO_2 were characterized for several of the sites that had more than 90 days of co-occurrences. For example, in 1978, Hamilton Co., Ohio, experienced 92 days with co-occurrences (18 complex-sequential and 74 sequential-only). In 1979 and 1980, Rubidoux, California reported 103 days with co-occurrences (67 complex-sequential and 36

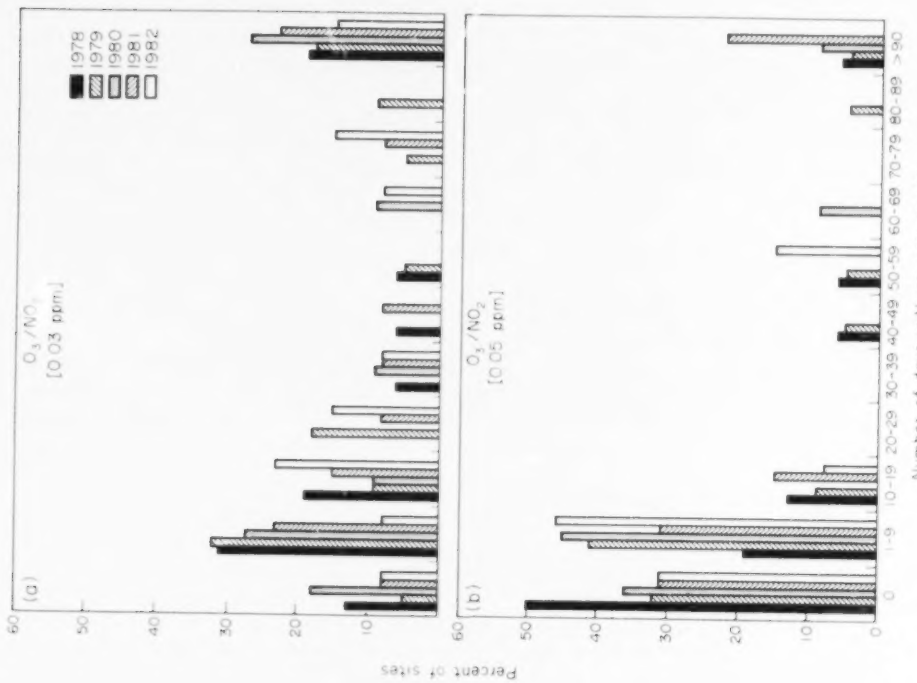

Fig. 5. Daily co-occurrence patterns of O_3/NO_2 for May–September: (a) at a concentration ≥ 0.03 ppm; (b) at a concentration ≥ 0.05 ppm.

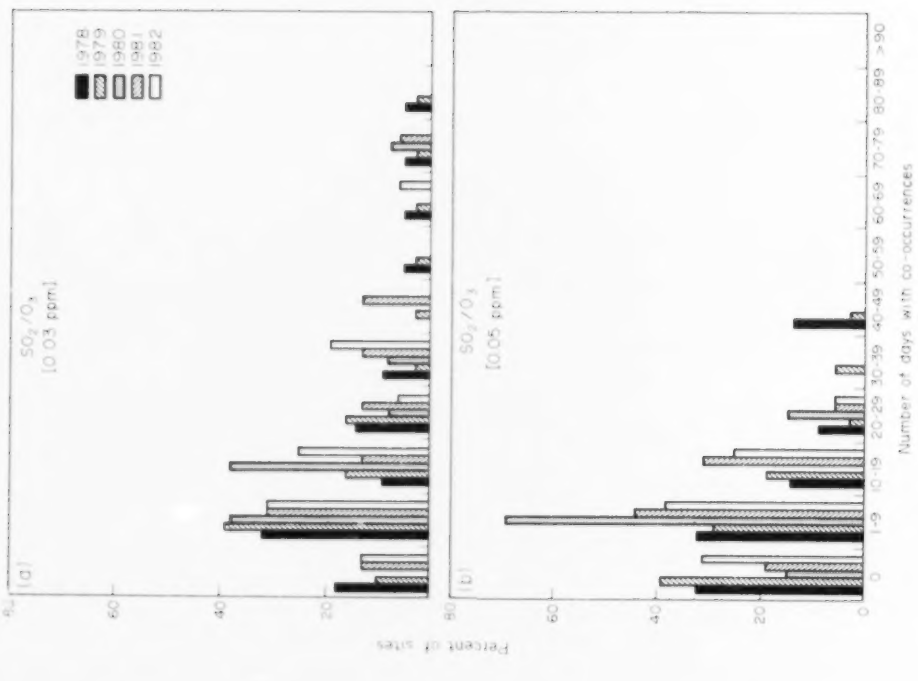

Fig. 4. Daily co-occurrence patterns of SO_2/O_3 for May–September: (a) at a concentration ≥ 0.03 ppm; (b) at a concentration ≥ 0.05 ppm.

sequential-only) and 100 days with co-occurrences (64 complex-sequential and 36 sequential-only), respectively. None of the sites experienced a daily simultaneous-only co-occurrence. For these monitoring sites, no clear preference for sequential-only vs complex-sequential co-occurrence was found. Modifying the minimum concentration to 0.07 ppm NO_2 and 0.03 ppm O_3 did not substantially change the total days of co-occurrences associated with the Ohio and California monitoring sites.

3.3. *Hourly occurrences of individual pollutants*

Using 1981 air quality data, Lefohn and Tingey (1984) identified the frequency of hourly simultaneous co-occurrences for co-monitored sites in the SAROAD data base. The hourly co-occurrence pattern at each monitoring site was characterized to identify whether (1) the frequency of hourly simultaneous co-occurrences increased substantially when the minimum concentration was lowered from 0.05 to 0.03 ppm and (2) any year-to-year variability might modify the authors' conclusions.

In our analysis performed over a multiple-year period, we found that SO_2 and NO_2 concentrations rarely reached levels ≥ 0.03 or 0.05 ppm. O_3 predominated when the number of occurrences of hourly concentrations at or above a minimum level was compared to the number of occurrences of hourly concentrations of SO_2 and NO_2 at or above a similar level. For example, using 1978 data, O_3 occurred on the average, at or above the 0.03 ppm level, 49.7% of the total number of hours over the 5-month period. Using the same minimum concentration, hourly concentrations of SO_2 occurred 2.8% of the time and NO_2, 8.0% of the time. Because the frequency of the number of hours that individual pollutants at concentrations $\geq$ a minimum concentration occur limits the number of possible hourly simultaneous co-occurrences, the number of hours that the pollutant pairs simultaneously co-occurred was small.

3.4. *Hourly simultaneous co-occurrences of pollutant pairs*

Using a minimum concentration of 0.03 ppm for the SO_2/NO_2 combination, 0–15% of the sites experienced more than 79 (2% of the total number of hours over a 5-month period) hourly simultaneous co-occurrences (Fig. 6a) for any given year. When the minimum concentration was raised to a 0.05 ppm, the number of hourly simultaneous co-occurrences decreased; none of the sites experienced >79 hourly simultaneous co-occurrences.

For SO_2/O_3, 6–27% of the sites experienced more than 79 hourly simultaneous co-occurrences using a minimum concentration of 0.03 ppm (Fig. 6b). When the minimum concentration was raised to 0.05 ppm,

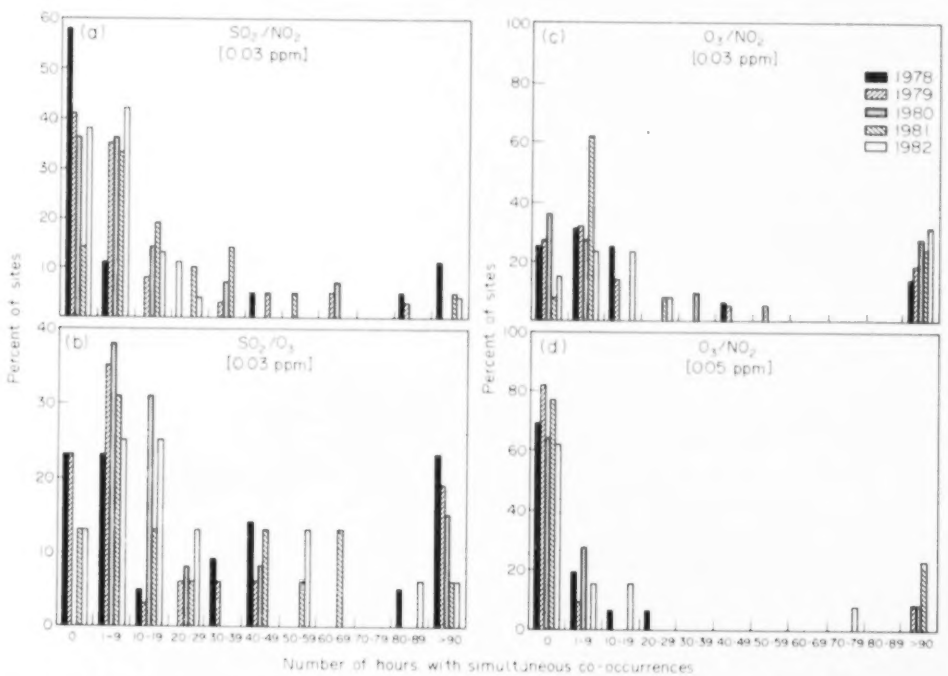

Fig. 6. Hourly co-occurrence patterns for May–September for: (a) SO_2/NO_2 at a concentration ≥ 0.03 ppm; (b) SO_2/O_3 at a concentration ≥ 0.03 ppm; (c) O_3/NO_2 at a concentration ≥ 0.03 ppm; (d) O_3/NO_2 at a concentration ≥ 0.05 ppm.

none of the sites experienced >79 h of simultaneous co-occurrences.

Applying a minimum concentration of 0.03 ppm for the O_3/NO_2 combination, 13–28% of the sites experienced more than 79 h of simultaneous co-occurrences (Fig. 6c). When the minimum concentration was raised to 0.05 ppm, 0–23% of the sites experienced >79 hourly simultaneous co-occurrences (Fig. 6d). All of the sites with 90 or more hourly simultaneous co-occurrences were located in the California South Coast Air Basin.

4. DISCUSSION

For most of the rural and remote monitoring sites characterized in this study, hourly SO_2 and NO_2 concentrations equal to or above 0.03 and 0.05 ppm occurred infrequently. Thus, it would be expected that the number of hours and days of co-occurrences of SO_2/NO_2 would be small. Our results confirm this trend. Year-to-year variation was insignificant at the 0.05 level; most sites experienced few co-occurrences of SO_2/NO_2 over the 5-year period.

Our results complement the findings reported by several investigators. Lefohn and Tingey (1984), using a minimum concentration of 0.05 ppm, the higher value used in our analysis, found that the number of hourly SO_2/NO_2 co-occurrences was rare. Jacobson and McManus (1985), studying air quality data from an area of the Ohio River Valley that contains four coal-fired power plants, found that the hourly simultaneous co-occurrence of SO_2 and NO_x was infrequent. Using minimum concentrations of 0.05 ppm and 58 $\mu g\ m^{-3}$ for SO_2 and NO_x, respectively, the authors showed that the two gases simultaneously co-occurred for less than 1% of the total hours monitored. Lane and Bell (1984), using air monitoring data from central London, England, reviewed 3 months (January–March) of hourly concentration data for SO_2, NO_2, NO and NO_x, and found that the co-occurrence of SO_2 and NO_2 hourly concentrations was infrequent. When a minimum concentration of 0.05 ppm was applied, the simultaneous occurrence of both pollutants was less than 1% of the monitoring period.

SO_2 and NO_2, because of their infrequent occurrence at hourly concentrations at or above 0.03 ppm, were the limiting pollutants controlling the number of possible co-occurrences with O_3 (i.e. SO_2/O_3 and O_3/NO_2). Our analysis showed that the number of co-occurrences of SO_2/O_3 and O_3/NO_2 was not as small at the 0.03 ppm level as we observed for the SO_2/NO_2 mixtures (Table 3).

Lefohn and Jones (1986) have reported that O_3 occurs frequently at many rural and remote monitoring sites in the United States at concentrations equal to or greater than 0.03 ppm and our analyses of data from rural and remote sites verify this observation. Even with the application of such a low minimum O_3 concentration (e.g. 0.03 ppm), the number of SO_2/O_3 and O_3/NO_2 co-occurrences was small.

The pollutant pair O_3/NO_2 co-occurred more often than the other two pollutant pairs. O_3 is formed during atmospheric photochemical reactions between nitrogen oxides and unsaturated organic compounds. The frequency of co-occurrence of the O_3/NO_2 pollutant pair would be expected to be closely tied to these atmospheric processes.

Our selection of the period May–September for the current analysis was based on our interest in characterizing ambient pollutant mixture exposures that agricultural crops might receive. Many of the monitors at the sites did not capture 100% of the hourly concentrations during the 5-month period. Our analyses were based on actual reported data. Assuming that the observed number of days with co-occurrences was representative of the May–September period, we determined the normalized days of co-occurrence for each pollutant pair to verify that our results would not have changed if data were collected for all days over the 153-day period. In all cases, the normalized number of co-occurrences for each pollutant pair was similar to the observed values because co-occurrences were so infrequent.

If the observation period had been extended to 12 months, the co-occurrence patterns might have been different. However, because O_3 concentrations are at their highest value during April–October, we would expect the co-occurrence patterns for SO_2/O_3 and O_3/NO_2 to be similar to the ones we have reported. We do not know if the number of SO_2/NO_2 co-occurrences would change, and caution is urged in extending our conclusions based on 5-month patterns to an annual basis.

The infrequent occurrence of pollutants at the minimum hourly concentrations used in our study resulted in the infrequent appearance of pollutant pair co-occurrences. Because of the rarity of these co-occurrences, the number of co-occurrences involving the three-pollutant mixture, $O_3/SO_2/NO_2$, would also be small. Most research investigators involved in mixture studies have assessed the effects of *hourly simultaneous co-occurrence exposures* on vegetation. There is a lack of research in which pollutant mixtures (1) mimic ambient concentrations and (2) reproduce realistic frequency of occurrences for *sequential* and *complex-sequential* co-occurrences.

Our analysis of ambient air quality data shows that the SO_2/NO_2, SO_2/O_3 and O_3/NO_2 co-occurrences at most rural and remote monitoring sites over the 5-month, summer period were infrequent. Year-to-year variability was found to be insignificant; most of the monitoring sites experienced co-occurrences of any type less than 12% of the 153 days. Based on our observations, we recommend that researchers attempting to assess the potential effects of SO_2/NO_2, SO_2/O_3 and O_3/NO_2 on vegetation in the U.S. should construct simulated exposure regimes so that (1) hourly simultaneous and daily simultaneous-only co-

occurrences are fairly rare and (2) when co-occurrences are present, complex-sequential and sequential-only co-occurrence patterns predominate.

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